

Chapter 2

Olefin Polymerization with Half-Metallocene Catalysts

Kotohiro Nomura and Jingyu Liu

Abstract In this chapter, recent development of half-sandwich titanium complexes containing anionic donor ligands as the catalyst precursors for olefin polymerization has been described. These catalysts display unique characteristics especially for synthesis of new ethylene copolymers by incorporation of new monomers that are very difficult or impossible to be incorporated in ethylene copolymerization by conventional Ziegler-Natta and ordinary metallocene catalysts. Both cyclopentadienyl fragment and anionic donor ligand play an essential key role for both the catalytic activity and the comonomer incorporation in the copolymerization.

2.1 Introduction

Polyolefins such as polyethylene [high density polyethylene (HDPE), linear low density polyethylene (LLDPE) etc.], polypropylene, produced by metal catalyzed olefin coordination polymerization, are important commercial synthetic polymers in our daily life, and the market capacity still increases every year [1–3]. Recently, considerable attention has been paid to produce new polymers with specified functions exemplified by COCs (cyclic olefin copolymer, optical materials) (See Reviews for cyclic olefin copolymers (See Reviews for cyclic olefin copolymers [4–9], syndiotactic polystyrene (thermal, chemical resistance) [10] and others. Since new polymers would be mostly prepared by incorporation of new comonomers (sterically encumbered, called *traditionally unreactive monomers* in

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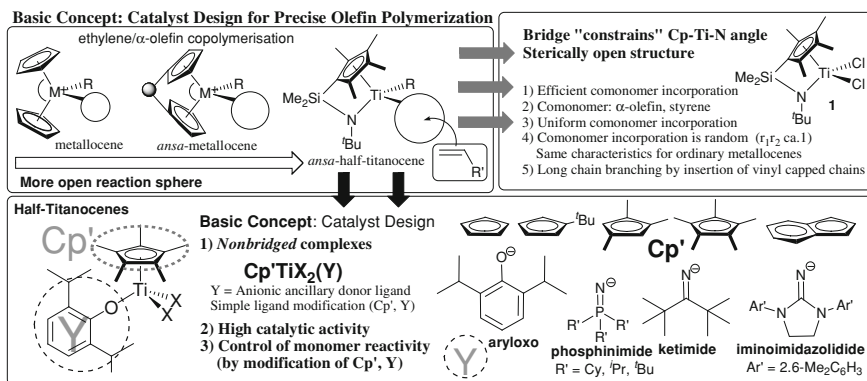
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transition metal catalyzed coordination polymerization) in the copolymerization, it has thus been considered that design of the efficient transition metal complex catalysts that precisely control olefin polymerization should be the key for the success; the new catalysts described herein offer promising possibilities (See Reviews for cyclic olefin copolymers [4–9], See Reviews for metallocenes [11–14], See Reviews for linked half-titanocenes [15–17], See Reviews for nonbridged half-titanocenes [18–20], See Reviews for post-metallocenes [18–24], See Selected reviews for (co)polymerization of polar monomers [25–27], See Selected reviews for living polymerization [28–42]).

It has been recognized that the catalysts exhibiting remarkable activities with better comonomer incorporations should be desired for the successful design of an efficient transition metal catalyst for ethylene (co)polymerizations. It has been reported that bridged (*ansa*) metallocene-type complexes generally show better comonomer incorporation than the nonbridged (unbridged) analogues in ethylene/ α -olefin copolymerization (See Reviews for metallocenes [11–14], Examples for ethylene/ α -olefin copolymerizations using metallocenes and constrained geometry type catalysts [43–45]). The fact has been explained as that the bridged metallocenes possess rather large coordination space compared to the nonbridged analogues, allowing better accessibility for (rather) bulky α -olefins (Scheme 2.1) (See Reviews for metallocenes [11–14]). Linked half-titanocenes containing amide ligand, $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ (**1**) so called “constrained geometry catalyst (CGC)”, have also been known to exhibit efficient comonomer incorporation (Scheme 2.1) [46–57], and the efficiency in α -olefin in ethylene/ α -olefin copolymerization, that can be evaluated by using r_E values under the similar conditions, increases in the order: $\text{Cp}_2\text{ZrCl}_2 < \text{rac-Me}_2\text{Si}[\text{benz(e)Ind}]_2\text{ZrCl}_2 < [\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{Ti-Cl}_2$ (**1**) (Examples for ethylene/ α -olefin copolymerizations using metallocenes and constrained geometry type catalysts [43–45]). This complex (CGC) was designed according to the analogous scandium complex [58, 59] and the reason for better comonomer incorporation has been explained as that *the bridge constrain more open Cp–Ti–N bond angle* offering better comonomer incorporation by allowing improved accessibility for (rather) bulky α -olefins (See Reviews for metallocenes [11–14], See Reviews for linked half-titanocenes [15–17]). Many researchers thus focused on designing the catalysts with “constrained geometry type” for the above reason (See Reviews for linked half-titanocenes [15–17, 46]).

2.2 Modified Half-Titanocenes as Olefin Polymerization Catalysts

Nonbridged half-titanocenes of the type, $\text{Cp}'\text{TiX}_2(\text{Y})$ (Cp' = cyclopentadienyl group; Y = anionic donor ligand such as aryloxo [60–66], ketimide [67–74], phosphinimide [75–77], iminoimidazolidide (Copolymerization with α -olefin containing bulky substituents [78–80]) etc.; X = halogen, alkyl), as shown in



Scheme 2.1 Basic proposed concept for the catalyst design for half-titanocenes [11–20]

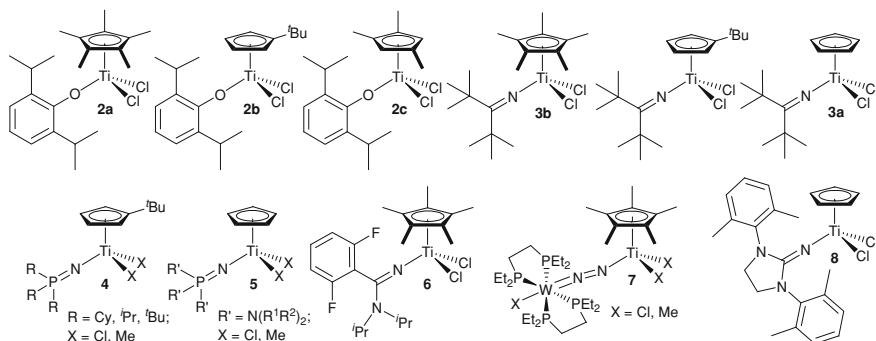
Scheme 2.2, have been considered as promising candidates for the efficient catalysts (Reviews for cyclic olefin copolymers [9], See Reviews for nonbridged half-titanocenes [18–20, 40–42], Our initial efforts in olefin polymerization and ethylene/ α -olefin copolymerization, for example [60–77, 81]), because these complex catalysts display unique characteristics especially for synthesis of new polymers (See Reviews for nonbridged half-titanocenes [19, 20], Ethylene copolymerization with 2-methyl-1-pentene (disubstituted α -olefin) [82, 83], Copolymerization with α -olefin containing bulky substituents [78–80], Copolymerization with norbornene [84–87], Copolymerization with cyclohexene, cyclopentene [88, 89], Copolymerization with styrene with efficient styrene incorporation or in a living manner [90–95]) that cannot be prepared (or are very difficult to be prepared) by ordinary catalysts such as Ziegler-Natta, metallocenes [11–14], ‘constrained geometry’ type catalysts (CGC) (See Reviews for linked half-titanocenes [15–17]. We reported in 1998 that half-titanocenes containing an aryloxo ligand of the type, $\text{Cp}'\text{TiCl}_2(\text{OAr})$ (Cp' = cyclopentadienyl group; OAr = aryloxo group, $\text{O-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3$ etc.), exhibited not only notable catalytic activities for olefin polymerization, but also for efficient 1-butene incorporation in the ethylene/1-butene copolymerization ([69], First patent application for Cp' -aryloxo complexes [96]; Related publications for synthesis and reactivity of cationic half-titanocene alkyl complexes containing aryloxo ligand [97–99]; See Related study (by the other group) concerning structure and activity correlation, effect of ion pairing and sterics on chain propagation for olefin polymerization by half-titanocenes containing aryloxides [100–102]). Therefore, there have been many examples concerning syntheses of complexes of this type and their use as olefin polymerization catalysts [19, 20], especially for ethylene polymerization. The selected examples in $\text{Cp}'\text{TiX}_2(\text{Y})$ that are known to be promising candidates as the efficient catalysts are shown in Scheme 2.2 (See Reviews for nonbridged half-titanocenes [18–20]; Our initial efforts in olefin polymerization and ethylene/ α -olefin copolymerization [60–66], [67–77, 81, 103–108].

2.2.1 Olefin Polymerization by Half-Titanocenes Containing Aryloxo Ligands

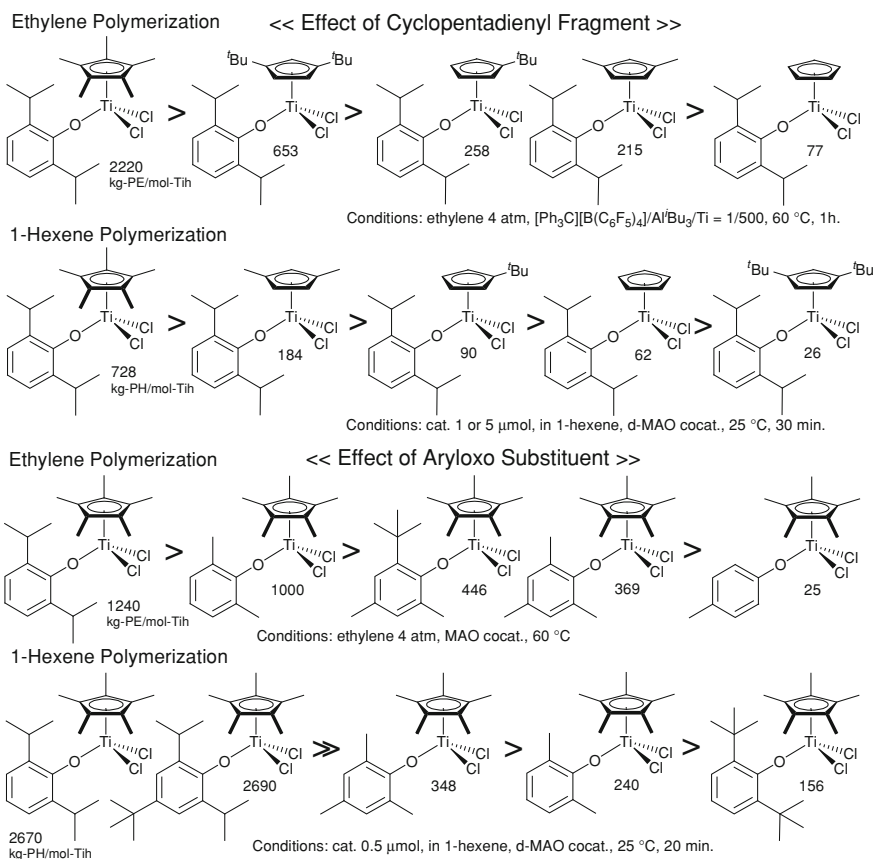
It has been known that the ligand modification is potentially important in order for metal catalyzed olefin polymerization to proceed with remarkable activities. For example, as shown in Scheme 2.3, substituents on both cyclopentadienyl and aryloxo ligands affect the activity for ethylene polymerization (Our initial efforts in olefin polymerization and ethylene/ α -olefin copolymerization, for example [60, 61]).

$\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**2a**) exhibited notable activities, and the activity by $\text{Cp}'\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ increased in the order: $\text{Cp}'=\text{Cp}^* \gg 1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3 > 1,3\text{-Me}_2\text{C}_5\text{H}_3, ^t\text{BuC}_5\text{H}_4 \gg \text{Cp}$. The similar trend was observed in the syndio-specific styrene polymerization using a series of $\text{Cp}'\text{Ti}(\text{OMe})_3$ complexes [40, 109, 110], and the fact would be assumed as due to a stabilization of the active site by more electron-donating substituents leading for the high activity. The $^t\text{Bu}_2\text{C}_5\text{H}_3$ analogue showed lower catalytic activity in 1-hexene and 1-octene polymerization due to the steric bulk on Cp' (See Our initial efforts in olefin polymerization and ethylene/ α -olefin copolymerization, for example [62, 64]). Steric bulk of the phenoxy ligand having substituents in the 2,6-position is important for exhibiting the high activity [1, 2]: this would play a role to stabilize the active species under the polymerization conditions in the presence of cocatalyst as well as to protect the probable side reaction with Al alkyls leading dissociation of the aryloxide (deactivation).

In order to explore the reason why both the Cp^* and 2,6-diisopropylphenoxy ligand in **2a** are prerequisite for the remarkable activity in the ethylene polymerization, structures of various Cp and aryloxide analogues were determined by X-ray crystallography [60, 61]. On the basis of structural data in $\text{Cp}'\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$, the bond angle (173.0°) of $\text{Ti}-\text{O}-\text{C}$ (phenoxy) for $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**2a**), which was the most effective catalyst precursor, is significantly different from those for the other Cp derivatives, ($\text{Cp}'=\text{Cp}$, $1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3$, $163.0\text{--}163.1^\circ$): the large $\text{Ti}-\text{O}-\text{C}$ bond angle would lead to more $\text{O} \rightarrow \text{Ti}$ π donation into Ti (Our initial efforts in olefin polymerization and ethylene/ α -olefin copolymerization, for example [60, 61]). However, the bond angle for the di-*tert*-butyl analogue, $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3)$, is small (155.5°): the bond angles of $\text{Ti}-\text{O}-\text{C}$ (phenyl) the diisopropyl analogues, ($173.0, 174.6^\circ$ for $\text{Ar}=2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$, $2,6\text{-}^i\text{Pr}_2\text{-}4\text{-}^t\text{BuC}_6\text{H}_2$, respectively) [60, 61, 111] are larger than those in the other Cp^* derivatives ($155.5\text{--}162.3^\circ$: $\text{Ar}=2,6\text{-Me}_2\text{C}_6\text{H}_3$, $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, $2,6\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3$, $2,6\text{-Ph}_2\text{C}_6\text{H}_3$ etc.) except $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-Ph}_2\text{-}3,5\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3)$ (176.9°) [97–99, 111]. Moreover, $\text{Cp}^*\text{Ti}(\text{X}^1)(\text{X}^2)(\text{O}-2,6\text{-}^i\text{Pr}_2\text{-}4\text{-R}'\text{C}_6\text{H}_2)$ ($\text{X}^1, \text{X}^2=\text{Cl}, \text{Cl}, \text{Me}, \text{Me}, \text{Me}, \text{CF}_3\text{SO}_3$, $\text{R}'=\text{H}$ or ^tBu) possessed relatively large bond angles in all cases ($166.2\text{--}174.6^\circ$). These results thus clearly suggest that the unique $\text{Ti}-\text{O}-\text{C}$ (phenyl) bond angle, leading to stabilize the catalytically-active species by more $\text{O} \rightarrow \text{Ti}$ π donation into the titanium, are dependent upon the substituents in both cyclopentadienyl and aryloxo ligands.



Scheme 2.2 Selected modified *nonbridged* half-titanocenes exemplified in this article as effective catalyst precursors



Scheme 2.3 Effect of cyclopentadienyl fragment (Cp') and aryloxo substituents toward the activity in olefin polymerization by $\text{Cp}'\text{TiCl}_2$ cocatalyst system

Simple calculations by geometry optimizations of the proposed catalytically active species, $[\text{Cp}'\text{Ti}(\text{penty})\text{(OAr)}(\text{ethylene})]^+$ (Fig. 2.1) with a series of cyclopentadienyl and aryloxo ligands, suggest that an introduction of methyl group (or *tert*-butyl group) onto Cp' leads to stabilization of the catalytically-active species ($\text{C}_5\text{Me}_5 > \text{Me}_3\text{C}_5\text{H}_2 > \text{Me}_2\text{C}_5\text{H}_2 > \text{C}_5\text{H}_5$) [109, 110]. The aryloxo substituent in the *ortho* position not only affects the stabilization, but also affects the R–Ti–ethylene bond angle that should be important for the subsequent insertion. It was thus revealed that the cationic species containing Cp* and diisopropylphenoxy ligands showed both better stabilization and possessed geometry for the subsequent insertion (narrow bond angle). Although the results are on the basis of simple PM3 semiempirical level, this would be considered as the origin why **2a** showed the high activity affording the polymer with unimodal distributions in this catalysis.

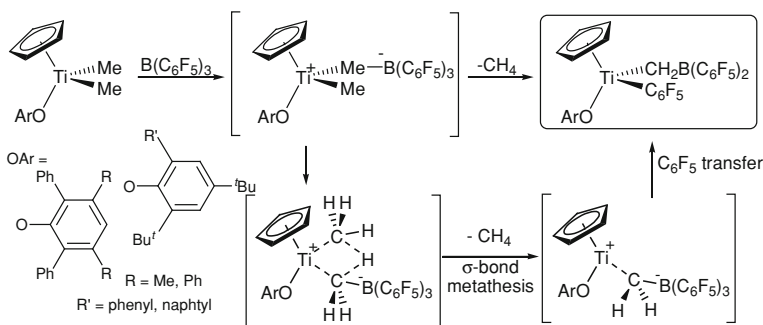
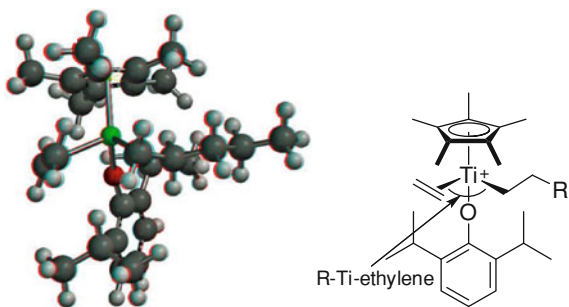
The observed activity was extremely low when 1-hexene polymerization was conducted in the presence of $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ and $\text{B}(\text{C}_6\text{F}_5)_3\text{-Al}^i\text{Bu}_3$, whereas the polymerization took place in a quasi-living manner with significant activity at $-30\text{ }^\circ\text{C}$ when $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ was used in place of $\text{B}(\text{C}_6\text{F}_5)_3$ [112]. The reaction with $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene-*d*₈ afforded decomposed compound, $\text{Cp}^*\text{Ti}(\text{C}_6\text{F}_5)[\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2](\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$, (and/or intermediates) even at $-70\text{ }^\circ\text{C}$, whereas no decomposition was observed if the reaction was employed with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ [113]. The species generated from the reaction consumed 1-hexene exclusively even at $-30\text{ }^\circ\text{C}$, suggesting that the generated cationic Ti(IV) species play a role in this catalysis.

Rothwell et al. also prepared a $\text{CpTiMe}_2(\text{OAr})$ complex containing an *ortho*-naphthylphenoxy ligand [97–99], and addition of $\text{B}(\text{C}_6\text{F}_5)_3$ in benzene gave thermally unstable cationic complex, $\text{CpTiMe}[(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3](\text{OAr})$, which then gradually decomposed at ambient temperature to afford the neutral species, $\text{CpTi}(\text{C}_6\text{F}_5)[\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2](\text{OAr})$, followed by methane elimination (Scheme 2.4) [97–99].

2.2.2 Selected Examples in Olefin Polymerization by Half-Titanocenes Containing the Other Anionic Ancillary Donor Ligands

Ligand effect toward the activity in ethylene polymerization using a series of half-titanocenes containing phosphinimide ligand of type, $\text{Cp}'\text{Ti}(\text{N}=\text{PR}_3)\text{X}_2$ (**4**, Table 2.1), were explored (Scheme 2.5) [75–77], because a sterically bulky $\text{N}=\text{PR}_3$ ligand as the steric equivalent to cyclopentadienyl group (Cp') [75–77] would provide the similar sterically/electronically environment to Cp' [114, 115]. These complexes exhibited remarkable activities in the presence of MAO, and the activity improved with the combination of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$: substituents on both Cp' and $\text{N}=\text{PR}_3$ ligands play a role for exhibiting the high activity, and use of $\text{N}=\text{PCy}_3$ ligand was

Fig. 2.1 Assumed catalytically-active species, the optimised structure [234]



Scheme 2.4 Deactivation pathway by reacting with $B(C_6F_5)_3$ [97–99]

Table 2.1 Ethylene polymerization by $Cp^*TiX_2(N=PR_3)$ [4, $Cp^*=Cp$, *tert*- BuC_5H_4 (tBuCp); $X=Cl$, Me; $R=Cy$, iPr , tBu —cocatalyst systems^a

Complex	Cocatalyst	Activity ^b	$M_w^c \times 10^{-4}$	M_w/M_n^c
$CpTiCl_2(N=P^tBu_3)$	MAO	500	8.99	2.4
$CpTiMe_2(N=P^tBu_3)$	$Ph_3CB(C_6F_5)_4$	401	16.6	3.4
$^tBuCpTiCl_2(N=P^tBu_3)$	MAO	881	6.54	2.4
$^tBuCpTiMe_2(N=PCy_3)$	$Ph_3CB(C_6F_5)_4$	1807	31	7.5
$^tBuCpTiMe_2(N=P^iPr_3)$	$Ph_3CB(C_6F_5)_4$	1193	25.9	9.9
$^tBuCpTiMe_2(N=P^tBu_3)$	$Ph_3CB(C_6F_5)_4$	1296	32.1	12.3
$[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$	MAO	630		

^a Cited from Ref. [75], Conditions catalyst 0.01–0.03 mmol, toluene, ethylene 1 atm, 25 °C, 0.5–3 min, MAO (Al/Ti = 500, molar ratio) or $Ph_3CB(C_6F_5)_4$ (B/Ti = 2)

^b Activity in kg-polymer/mol-Ti·h

^c GPC data in *o*-dichlorobenzene versus polyethylene standards

effective. The tBuC_5H_4 analogues were more suited than the Cp analogues, suggesting that electron-donating substituents on Cp^* increase the activity. Analogous zirconium complexes showed low activities for ethylene polymerization [116, 117]. The tris(amido)phosphinimide analogues, $Cp^*TiX_2[N=P(NR_2)_3]$ (5, $X=Cl$, Me), showed

Table 2.2 Ethylene polymerization by $\text{Cp}^*\text{TiX}_2[\text{NP}(\text{NR}^1\text{R}^2)_3]$ (**5**)—cocatalyst systems^a

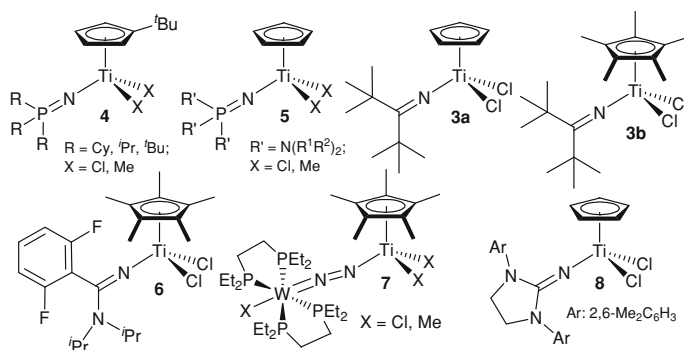
Complex ($\mu\text{mol L}^{-1}$)	Cocat.	Time /min	Activity ^b	$M_n^c \times 10^{-4}$	M_w/M_n^c
$\text{Cp}^*\text{TiCl}_2[\text{N}=\text{P}\{\text{N}(\text{EtPh})_3\}_3]$ (50)	MAO	30	200	12.61	4.02
$\text{CpTiMe}_2[\text{N}=\text{P}\{\text{N}(\text{EtPh})_3\}_3]$ (4)	Al/B ^d	10	4200	43.25	1.92
$\text{Cp}^*\text{TiMe}_2[\text{N}=\text{P}(\text{NMe}_2)_3]$ (4)	Al/B ^d	10	4200	14.08	4.92
$\text{Cp}^*\text{TiMe}_2[\text{N}=\text{P}(\text{NEt}_2)_3]$ (4)	Al/B ^d	10	4700		
$\text{Cp}^*\text{TiMe}_2[\text{N}=\text{P}(\text{NPr}_2)_3]$ (4)	Al/B ^d	10	10000		
$\text{Cp}^*\text{TiMe}_2[\text{N}=\text{P}\{\text{N}(\text{EtPh})_3\}_3]$ (4)	Al/B ^d	10	4200	32.46	2.03
$\text{Cp}^*\text{TiMe}_2[\text{N}=\text{P}^i\text{Pr}_3]$ (4)	Al/B ^d	10	5200	49.34	2.05
$\text{CpTiMe}_2[\text{N}=\text{P}^i\text{Bu}_3]$ (4)	Al/B ^d	10	5600	43.78	1.80
Cp_2ZrMe_2 (4)	Al/B ^d	10	16000	17.5	1.89

^a Cited from Ref. [103], Conditions ethylene 2 atm, 30 °C, toluene 600 mL, 1000 rpm, 500 equiv of MAO or Al/B

^b Activity in kg/mol-Ti·h·atm

^c GPC data in *o*-dichlorobenzene versus polyethylene standards

^d Al/B=Alⁱ Bu₃/B(C₆F₅)₃, 2 equiv of B(C₆F₅)₃; 20 equiv of Alⁱ Bu₃

**Scheme 2.5** Selected modified *nonbridged* half-titanocenes exemplified in this section

high activities in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ (Table 2.2) [103], and the activity increased upon increasing the steric bulk.

In contrast, no significant differences in the activities were observed in ethylene polymerization using $\text{Cp}^*\text{TiCl}_2(\text{N}=\text{C}^i\text{Bu}_2)$ ($\text{Cp}^*=\text{Cp}$, $^i\text{BuC}_5\text{H}_4$, Cp^*) [70], whereas the activities in 1-hexene polymerizations were affected by the Cp^* employed (Table 2.3) [70, 71]. 1-Hexene polymerization by $\text{CpTiCl}_2(\text{N}=\text{C}^i\text{Bu}_2)$ took place efficiently, and a first order relationship between the monomer concentration and the reaction rate was observed, strongly suggesting that the apparent decrease is due to the decrease in the 1-hexene concentration not due to a deactivation of the catalytically-active species. The activities by $\text{Cp}^*\text{TiCl}_2[\text{N}=\text{C}(\text{R}^1)\text{R}^2]$ were strongly affected by the ketimide substituents [69, 87], and the complexes containing two ^iBu groups as the ketimide substituents were effective to give polymers with unimodal molecular weight distributions, in other words, to proceed with uniform catalytically-active species.

Table 2.3 Ligand effect in ethylene polymerization by $\text{Cp}^*\text{TiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ ($\text{Cp}^*=\text{Cp}$, $^t\text{BuC}_5\text{H}_4$, Cp^* , indenyl)—MAO catalyst systems^a

Cp^* (μmol)	Olefin	Activity ^b	$M_w^c \times 10^{-5}$	M_w/M_n^c
Cp (0.2)	Ethylene	13400	9.66	1.9
$^t\text{BuC}_5\text{H}_4$ (0.2)	Ethylene	14300	9.9	2.1
Cp^* (0.2)	Ethylene	16600	10.4	2.2
Indenyl (0.2)	Ethylene	7700	5.61	2.1
Cp (0.25)	1-hexene	16800	6.17	1.6
$^t\text{BuC}_5\text{H}_4$ (2.5)	1-hexene	1310	2.85	1.7
Cp^* (2.5)	1-hexene	569	1.30	1.6
Indenyl (0.25)	1-hexene	11900	2.81	1.7

^a Cited from Refs. [70, 71], *Conditions* (ethylene) complex 0.2 μmol , toluene 40 mL, ethylene 4 atm, MAO white solid 3.0 mmol (Al), 40 °C, 10 min; *Conditions* complex in toluene 0.5 mL, 1-hexene 10 mL, 25 °C, 20 min, MAO white solid 2.0 mmol

^b Activity in kg-polymer/mol-Ti·h

^c GPC data in *o*-dichlorobenzene or THF versus polystyrene standards

$\text{Cp}^*\text{TiX}_2[\text{N}=\text{C}(2,6\text{-R}_2^1\text{C}_6\text{H}_3)(\text{NR}_2^2)]$ [6, Scheme 2.2, $\text{R}^1=\text{F}$, Cl ; $\text{R}^2=i\text{Pr}$, Cy etc.; $\text{X}=\text{Cl}$, Me] exhibited remarkable activities for ethylene/propylene copolymerization (for synthesis of EPDM, ethylene–propylene–diene copolymer) [104, 105], and the activity was highly affected by the substituents (R^1, R^2); $\text{Cp}^*\text{TiX}_2[\text{N}(2,6\text{-F}_2\text{C}_6\text{H}_3)(\text{N}^i\text{Pr}_2)]$ exhibited notable activity [104]. Ethylene polymerization and copolymerization of ethylene with 1-hexene catalyzed by heterobimetallic dinitrogen complex (7, Scheme 2.5) were reported [106]. The complex exhibited high activities, but the 1-hexene incorporation was not sufficient probably due to bulky substituent in the anionic donor ligand.

Half-titanocenes containing iminoimidazolidide ligand, $\text{CpTi}(\text{CH}_2\text{Ph})_2[1,3\text{-(2,6-Me}_2\text{C}_6\text{H}_3)_2\text{-(CH}_2\text{N)}_2\text{C}=\text{N}]$ (8, Scheme 2.5) exhibited notable activities for ethylene polymerization in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ cocatalyst [81]. The catalyst was reported to show higher activities than the $\text{CpTi}(\text{CH}_2\text{Ph})_2(\text{NP}^t\text{Bu}_3)$ under the same conditions (in the presence of partially hydrolyzed Al^iBu_3 , TIBAO). However, comonomer incorporations in the copolymerization of ethylene with α -olefin, styrene, norbornene were not as high as those by the aryloxo [60–66, 90–95] or ketimide analogues [84–87]. Taking into account the facts described above, the role of anionic donor ligand should be the key for design of more effective catalyst precursors in this catalysis.

2.2.3 Copolymerizations of Ethylene with Sterically Encumbered α -olefins

2.2.3.1 Copolymerizations of Ethylene with Linear α -olefins

Table 2.4 summarizes selected results in copolymerizations of ethylene with α -olefins using $\text{Cp}^*\text{TiCl}_2(\text{O-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (2a), $\text{CpTiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ (3a), and the

Table 2.4 Selected results in ethylene copolymerization with 1-hexene, 1-dodecene by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**2a**), $\text{CpTiCl}_2(\text{N}=\text{C}^i\text{Bu}_2)$ (**3a**), $[\text{Me}_2\text{Si}(\text{C}_3\text{Me}_4)(\text{N}^i\text{Bu})]\text{TiCl}_2$ (**1**)-MAO catalyst systems^a

Complex (μmol)	Comonomer ^b (M)	Ethylene /atm	Temp/ $^{\circ}\text{C}$	Activity ^c	$M_n^d \times 10^{-5}$	M_w/M_n^d	Cont. ^e /mol%
$\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (2a) (0.08)	1-hexene (0.73)	7	40	103000	2.30	1.98	24.6
$\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (2a) (0.07)	1-hexene (1.45)	7	40	263000	1.80	1.87	38.1
$[\text{Me}_2\text{Si}(\text{C}_3\text{Me}_4)(\text{N}^i\text{Bu})]\text{TiCl}_2$ (1) (0.60)	1-hexene (0.73)	7	40	14600	5.17	2.30	23.7
$[\text{Me}_2\text{Si}(\text{C}_3\text{Me}_4)(\text{N}^i\text{Bu})]\text{TiCl}_2$ (1) (0.65)	1-hexene (1.45)	7	40	6960	3.98	2.21	39.4
$\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (2a) (0.01)	1-dodecene (0.75)	6	25	230000	1.87	1.99	19.2
$\text{CpTiCl}_2(\text{N}=\text{C}^i\text{Bu}_2)$ (3a) (0.01)	1-dodecene (0.75)	6	25	123000	4.84	1.97	15.5
$[\text{Me}_2\text{Si}(\text{C}_3\text{Me}_4)(\text{N}^i\text{Bu})]\text{TiCl}_2$ (1) (0.10)	1-dodecene (0.75)	6	25	24800	3.91	2.09	19.2

^a Cited from Refs. (Our initial efforts in olefin polymerization and ethylene/ α -olefin copolymerization, for example, [60–66]), Conditions toluene and comonomer total 30 mL, dried MAO (prepared by removing toluene and AlMe_3 from the ordinary MAO) 3.0 (or 2.0) mmol, 25 $^{\circ}\text{C}$, 10 min

^b Initial comonomer concentration in mmol/mL

^c Activity in kg-polymer/mol-Ti·h

^d GPC data in *o*-dichlorobenzene versus polystyrene standards

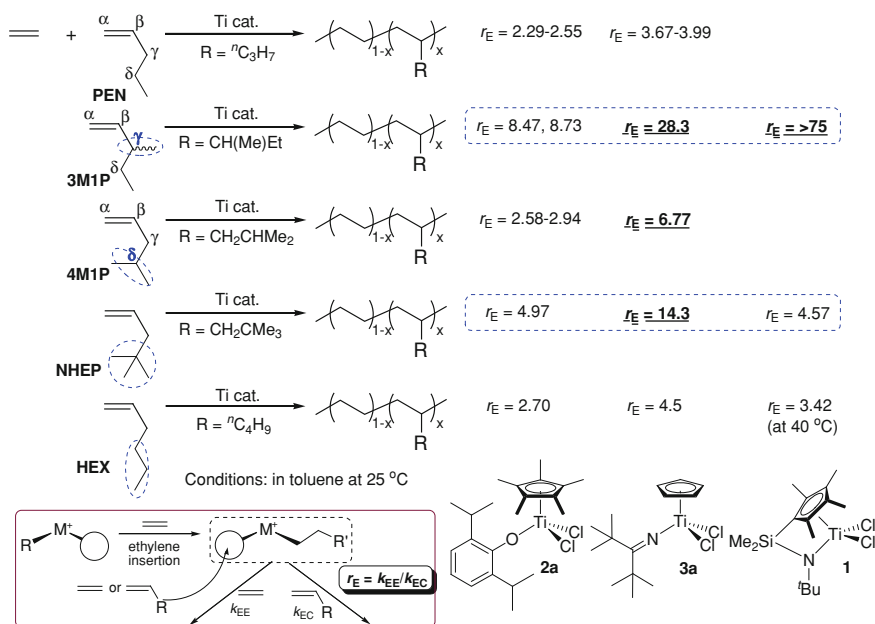
^e Comonomer contents estimated by ^{13}C NMR spectra

^f Cited from Ref. [61], polymerization for 6 (or 4) min

constrained geometry catalyst (CGC), $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ (**1**), in the presence of MAO cocatalyst [63, 64, 71, 80]. The Cp^* -aryloxo analogue (**2a**) exhibited remarkable activities for copolymerization of ethylene with 1-butene [61], 1-hexene [63, 64], and 1-decene [80] affording high molecular weight copolymers with uniform compositions. The observed activities (calculated from the polymer yields) by **2a** were higher than those by **1**, and the 1-hexene contents in the resultant copolymers by **2a** were close to those by **1** under the same conditions [63, 64]. The activity by **2a** increased upon increasing the 1-hexene concentration, whereas the activity by CGC (**1**) decreased upon increasing 1-hexene concentration [64]. The $^t\text{BuC}_5\text{H}_4$ analogue, $(^t\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6-^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**2b**), showed better 1-hexene incorporation than **2a**, whereas the $^t\text{Bu}_2\text{C}_5\text{H}_3$ analogue showed the less efficient incorporation.

The Cp -ketimide analogue (**3a**) also exhibited high activities in the copolymerizations [71], but the comonomer incorporations were less efficient than those by **2a** and **1**, suggesting that the comonomer incorporation was affected by the anionic donor ligand. The activities by the Cp^* -ketimide analogue, $\text{Cp}^*\text{TiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ (**3b**), exhibited better catalyst performance than **3a** under high temperature (160 °C) and high pressure (1500 psi, 102 atm), continuous solution polymerization conditions [69].

Effect of the centered metal toward the activity and the comonomer incorporation were explored in ethylene (co)polymerization using a series of $\text{Cp}^*\text{MCl}_2(\text{O}-2,6-\text{R}_2\text{C}_6\text{H}_3)$ ($\text{M}=\text{Ti}, \text{Zr}, \text{Hf}; \text{R}=\text{Ph}, ^t\text{Bu}$) in the presence of MAO cocatalyst [118]. The activity in ethylene polymerization was affected by the centered metal employed [$\text{Ti} > \text{Zr} > \text{Hf}$]; the phenyl analogues ($\text{R}=\text{Ph}$) showed higher activities than the *tert*-butyl analogues ($\text{R}={}^t\text{Bu}$). The ethylene/1-octene copolymerizations afforded copolymers with uniform molecular weight distributions, except $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6-^t\text{Bu}_2\text{C}_6\text{H}_3)$, where both the activity and the 1-octene incorporation were highly affected greatly by the centered metal employed: $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6-^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**2a**) was the most suitable in terms of both activity and the 1-octene incorporation. The attempted copolymerization of ethylene with 2-methyl-1-pentene (2M1P) using the above complexes—MAO catalysts afforded linear polyethylene, whereas **2a** incorporated 2M1P under the same conditions [118]. The copolymerizations by $(1,3-\text{Me}_2\text{C}_5\text{H}_3)\text{TiCl}_2(\text{O}-2,6-^i\text{Pr}_2\text{C}_6\text{H}_3)$, $\text{CpTiCl}_2(\text{O}-2,6-^i\text{Pr}_2\text{C}_6\text{H}_3)$, $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6-\text{Me}_2\text{C}_6\text{H}_3)$ and $(1,3-^t\text{Bu}_2\text{C}_5\text{H}_3)\text{TiCl}_2(\text{O}-2,6-\text{Me}_2\text{C}_6\text{H}_3)$ afforded polymers with bimodal molecular weight distributions, whereas the resultant copolymers possessed uniform molecular weight distributions in the copolymerizations by the Cp^* -aryloxo analogue (**2a**), $^t\text{BuC}_5\text{H}_4$ analogue (**2b**), and $^t\text{Bu}_2\text{C}_5\text{H}_3$ analogue [64]. Therefore, effect of ligand substituents plays an essential role in the ethylene copolymerization by $\text{Cp}^*\text{TiCl}_2(\text{OAr})$ —MAO catalyst systems not only exhibiting high catalytic activity, but also affording high molecular weight copolymer with uniform distribution [64].



Scheme 2.6 Copolymerization parameters (r values) in ethylene copolymerizations using half-titanocenes [80]

2.2.3.2 Copolymerizations of Various Substituted Pentenes

Effect of structure/ligand toward both the catalytic activities and the monomer reactivities in the ethylene copolymerizations with various pentenes [1-pentene, 4-methyl-1-pentene (4M1P), 3-methyl-1-pentene (3M1P, mixture of *R* and *S*), 4,4-dimethyl-1-pentene (NHEP)] using the Cp*-aryloxo analogue (**2a**), the Cp-ketimide analogue (**3a**), the constrained geometry catalyst (**1**) were conducted in the presence of MAO. Scheme 2.6 summarizes r_E , r_C (E = ethylene, C = comonomer) and $r_E \cdot r_C$ values for the copolymerizations by the Cp*-aryloxo analogue (**2a**), the Cp-ketimide analogue (**3a**) and CGC (**1**) based on experimental results (in toluene at 25 °C).

The Cp*-aryloxo analogue (**2a**) exhibited both remarkable catalytic activity and efficient 3M1P incorporation in the ethylene/3M1P copolymerization; the r_E value (8.73) was much smaller than those by **1** (92), **3a** (28.3). Both **2a** and **1** showed better NHEP incorporation than **3a** in the ethylene/NHEP copolymerization; the rather large r_E value by **3a** (6.77) compared to those by **2a** (2.58–2.94) was also obtained in the copolymerization with 4M1P [80]. The results suggest that the monomer reactivity by **3a** was influenced by the substituent in the δ -position (in addition to the substituent in the γ -position), whereas the monomer reactivity by **1** was more influenced by the substituent in the γ -position (Scheme 2.6). The monomer reactivities (r_E values) are thus strongly influenced not only by both the substituent in the olefins and the (electronic and steric) nature of the catalytically

active species (structure, ligand set employed). The $r_E \cdot r_C$ values by **2a** were small in all cases, suggesting that the comonomer incorporations were rather alternating, whereas the copolymerization by **1** proceeded in a random manner (comonomer incorporations were random, $r_E \cdot r_C \approx 1$) except the copolymerization with 3M1P. The observed differences emphasize unique characteristics for using this half-titanocenes for precise olefin copolymerization [19, 63, 64, 71, 80].

2.2.3.3 Copolymerizations of Ethylene with 2-methyl-1-Pentene

Synthesis of ethylene copolymers containing 2,2-disubstituted-1-olefins is one of the promising targets, because only a few examples were known in the metal catalyzed olefin polymerization [119]. For example, ethylene/isobutene (IB) copolymerization using $[(CH_2CH_2)(indenyl)_2]ZrCl_2$ —MAO catalyst system afforded a copolymer with low IB content (<2.8 mol%) even under large IB stoichiometric excess conditions (IB:ethylene = 4000:1) [120]. The resultant copolymer in the ethylene/2-methyl-1-pentene (2M1P) copolymerization by $[Me_2Si(MeC_5H_3)(N\text{-cyclododecyl})]TiMe_2$ — $[PhN(H)Me_2][B(C_6F_5)_4]$ catalyst system, possessed low molecular weight with broad molecular weight distributions ($M_n = 10780$, $M_w/M_n = 5.9$, 2M1P content 9.0 mol%) [121], although the ethylene/IB copolymerization (MAO cocatalyst) afforded a copolymer with 45 mol% IB content under certain conditions (ethylene 0.34 bar, $M_n = 13200$, $M_w/M_n = 2.5$) [121].

Notable improvement in the IB incorporation (30 times increase in the IB/ethylene reactivity ratio) had recently been achieved by using a binuclear constrained geometry type half-titanocene in the presence of a bifunctional borate cocatalyst (Scheme 2.7) [122, 123], and it was proposed that the increased selectivity for highly encumbered comonomer enchainment, presumably facilitated via cooperative comonomer capture/binding/delivery by the proximate cationic centers ([122], Reviewing article for nuclearity and cooperativity effects in binuclear catalysts and cocatalysts for olefin polymerization [123, 124]. However, both the activity and the IB incorporation were sensitive to the cocatalyst and the activity was slightly decreased upon increasing the catalyst/cocatalyst nuclearity (Table 2.5).

Copolymerization of ethylene with 2M1P using the Cp^* -aryloxo analogue (**2a**)—MAO catalyst system took place with rather efficient 2M1P incorporation (Table 2.6), whereas the 2M1P incorporations by Cp_2ZrCl_2 , $[Me_2Si(C_5Me_4)(N^t\text{-Bu})]TiCl_2$ (**1**), $Cp^*TiCl_2(N=C^tBu_2)$ [$Cp^*=Cp$ (**3a**), Cp^* (**3b**)—MAO catalyst systems were negligible under the same conditions. Effect of ligand substituents toward the catalytic activities and the 2M1P incorporations were also explored, and use of both Cp^* and 2,6-diisopropylphenoxy ligands were found to be important to obtain a copolymer with a rather efficient and uniform 2M1P incorporation as well as with moderate catalytic activities. No distinct differences in 2M1P incorporations were seen in the copolymerization by **2a** in the presence of various cocatalysts [methylaluminumoxane (MAO), methyl-isobutyl-aluminumoxanes (modified MAO,

Scheme 2.7 Typical dinuclear catalyst/cocatalyst systems in ethylene copolymerizations [122, 123]

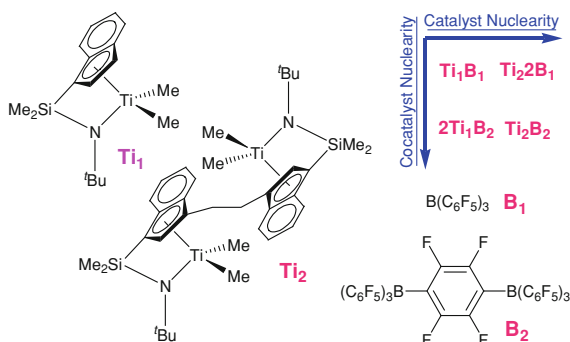


Table 2.5 Copolymerization of ethylene with isobutene (IB) catalyzed by binuclear (co)catalysts^a

Cat. (μmol)	Cocat.	Time /min	Activity ^b	$M_w^c \times 10^{-5}$	M_w/M_n^c	Cont. ^d /mol%
Ti₁ (10)	B₁	5	960	5.77	2.13	3.1
Ti₁ (10)	B₂	5	440	3.05	2.16	9.5
Ti₂ (5)	B₁	10	360	4.90	2.41	7.3
Ti₂ (5)	B₂	10	280	1.68	3.67	15.2
Ti₁ (10)	MAO^c	60	39	4.87	2.52	2.9
Ti₂ (5)	MAO^c	240	11	3.55	2.87	6.2

^a Cited from Refs. [122, 123], *Conditions* Polymerizations carried out on a high-vacuum line at 24 °C in 100 mL of toluene under 1.0 atm ethylene pressure, isobutene 1.2 mmol/mL (M)

^b Activity in kg-polymer/mol-Ti

^c GPC data in *o*-dichlorobenzene versus polystyrene standards

^d Estimated from ¹³C NMR spectra

^e Al:Ti = 1000:1

Table 2.6 Copolymerization of ethylene with 2-methyl-1-pentene (2M1P) by Cp*TiCl₂(Y) [Y=O-2,6-*i*Pr₂C₆H₃, Cp*=Cp* (**2a**) *t*BuC₅H₄ (**2b**); Y=N=CⁱBu₂, Cp*=Cp (**3a**), Cp* (**3b**), [Me₂Si(C₅Me₄)(NⁱBu)]TiCl₂ (**1**), Cp₂ZrCl₂–MAO catalyst systems^a

Cat. (μmol)	Ethylene /atm	Activity ^b	$M_n^c \times 10^{-4}$	M_w/M_n^c	2M1P ^d /mol%
2a (0.5)	6	5760	10	1.8	5.7
2a (0.5)	4	2680	4.9	1.6	9.4
2b (2.0)	4	324	1.8	2.3	5.1
3a (0.2)	6	6960	34	1.8	0.3
3b (0.2)	6	7770	63	1.9	0.3
1 (1.0)	6	1840	12	2.4	0.3
Cp₂ZrCl₂ (0.2)	6	4590	148	2.7	trace

^a Cited from Ref. [70], *Conditions* 2M1P 2.70 mmol/mL, 2M1P + toluene total 30 mL, d-MAO 3.0 or 4.5 mmol, 25 °C, 6 or 10 min

^b Activity in kg-polymer/mol-M·h (M=Ti, Zr)

^c GPC data in *o*-dichlorobenzene versus polystyrene standards

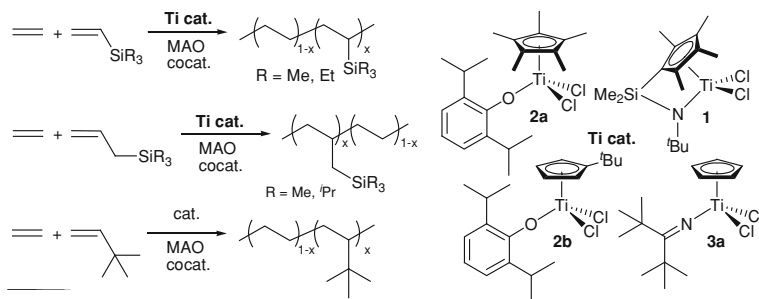
^d 2M1P in copolymer (mol%) estimated by ¹³C NMR spectra

MMAOs), borates], and the nature of the ligands thus predominantly affects the 2M1P incorporation. The 2M1P contents in the copolymers prepared by the $t\text{-BuC}_5\text{H}_4\text{-aryloxo}$ analogue (**2b**) were lower than those by **2a** under the same conditions, whereas **2b** exhibited better 1-hexene incorporation than **2a** in the ethylene/1-hexene copolymerization [63, 64]. On the basis of the calculation of the optimised geometries for assumed catalytically-active [cationic Ti(IV) alkyl] species after 2M1P insertion [93, 94], this may be explained as due to the steric hindrance of *tert*-butyl group on Cp' against the methyl group in Cp* (difference in the stabilization of ethylene coordination after insertion of 2M1P) [125].

2.2.3.4 Copolymerization of *Tert*-butylethylene, α -olefins Containing Trialkylsilyl Group

Precise, efficient functionalization of polyolefins under mild conditions is considered as an attractive subject, and the controlled incorporation of the desired functionalities by the direct copolymerization has been one of the most promising approaches (See Selected reviews for (co)polymerization of polar monomers (Selected reviews for (co)polymerization of polar monomers: [25, 32], See Book and reviews [126–129], See Recent examples for transition metal catalyzed coordination copolymerization with monomers containing polar functionalities [130–137], Examples for late transition metal catalysts [138–141], Selected examples (ATRP, Nitroxide, RAFT etc.) [142–152]). However, the introduction in the copolymerization of ethylene or propylene with (protected) polar monomer(s) faces difficulties due to catalyst poisoning as well as to the interaction of the centered metal with the functional groups. The copolymerizations of ethylene with certain alkenylsilanes [$\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{SiH}_3$, $n = 1, 2, 4, 6$ etc.] using (dinuclear) linked half-titanocenes have been known as a promising route [153, 154], but the activity generally decreased upon increasing the comonomer content(s); the silane(s) also play a role as the chain transfer reagent(s) [154]. The copolymerization of ethylene with allyltrimethylsilane (ATMS) by certain metallocenes was also known (Chain transfer by Si [155–159]), but both the activities and the M_n values in the copolymers decreased depending on the ATMS contents. This is because ATMS also plays the role of chain transfer reagent due to a favored β -hydrogen elimination after bulky ATMS insertion (Previous reports for polymerization of ATMS by metallocenes [160, 161]).

The copolymerization with ATMS by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)$ (**2a**) proceeded efficiently, affording high molecular weight copolymers with uniform molecular weight distributions (Scheme 2.8, Table 2.7) [162, 163]. The activity by **2a** increased upon increasing the initial ATMS concentration and/or ethylene pressure. The Cp-ketimide analogue, $\text{CpTiCl}_2(\text{N}=\text{C}^i\text{Bu}_2)$ (**3a**) showed less efficient ATMS incorporation in the copolymerization under the same conditions, but exhibited much higher catalytic activity than **2a**, affording high molecular weight copolymers with unimodal molecular weight distributions. The activity increased



Scheme 2.8 Copolymerizations of ethylene with vinyltrimethylsilane (VTMS), allyltrimethylsilane (ATMS), and with *tert*-butyl ethylene (TBE) [79, 162, 163]

Table 2.7 Copolymerization of ethylene with $\text{CH}_2=\text{CHCH}_2\text{SiMe}_3$ (ATMS), $\text{CH}_2=\text{CHSiMe}_3$ (VTMS), and with *tert*-butylethylene (TBE) using $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ [$\text{Cp}^*=\text{Cp}^*$ (**2a**), $t\text{BuC}_5\text{H}_4$ (**2b**)], $\text{CpTiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ (**3a**), $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ (**1**), and Cp_2ZrCl_2 —MAO catalyst systems^a

Complex (μmol)	Comonomer (M)	Ethylene / atm	Activity ^b	$M_n^c \times 10^{-4}$	M_w/M_n^c	Cont. ^d / mol%
2a (0.50)	ATMS (1.05)	6	3550	2.78	2.7	48.8
2a (0.50)	VTMS (1.15)	6	1870	30.5	1.9	5.1
2b (0.20)	VTMS (1.15)	6	92	1.41	2.8	13.6
3a (0.05)	ATMS (1.05)	6	47500	28.3	2.6	30.3
3a (1.00)	VTMS (1.15)	6	3730	57.3	2.3	11.9
1 (0.25)	VTMS (1.15)	6	2280	36.7	2.5	10.4
Cp_2ZrCl_2 (10.0)	VTMS (1.15)	6	23	0.56	3.9	trace
2a (0.20)	TBE (3.9)	2	2880	20.4	2.0	1.7
2b (1.00)	TBE (3.9)	2	1130	5.31	2.1	6.3
2b (1.00)	TBE (3.9)	4	2020	8.17	2.4	3.3
3a (0.40)	TBE (3.9)	2	1880	13.9	1.9	trace
1 (1.00)	TBE (3.9)	2	1190	11.9	2.1	none
Cp_2ZrCl_2 (0.05)	TBE (3.9)	2	24300	56.3	2.4	none

^a Cited from Refs. [79, 162] and [163], conditions (AMTS, VMST) comonomer 10 mL; comonomer + toluene total 30.0 mL, dried MAO 3.0 mmol, ethylene 6 atm, 25 °C; 10 min; conditions (TBE) ethylene 2 atm, TBE 5.0 mL, toluene 5.0 mL, dried MAO 5.0 mmol, 25 °C, 10 min

^b Activity in kg-polymer/mol-M-h (M=Ti, Zr)

^c GPC data in *o*-dichlorobenzene versus polystyrene standards

^d Comonomer content estimated by ^{13}C NMR spectra

upon increasing the ATMS concentration and the ethylene pressure, and the M_n values in the copolymers were independent of the ATMS contents.

Vinyltrialkylsilanes should be considered as better comonomers in terms of the direct functional group introduction into the polyethylene (or polypropylene) backbone as well of their use as cross-linking reagents to improve thermal properties (See Preparation of poly(vinylsilane)s [164–166]). These sterically

encumbered olefins are, however, very difficult to coordinate into the metal center in ordinary metallocenes (Equilibrium constants for alkene coordination to $(\text{MeC}_5\text{H}_4)_2\text{Zr}^+(\text{O}^t\text{Bu})(\text{ClCD}_2\text{Cl})$ [167]), and no reports for the copolymerization had been published until recently (See For reported examples of insertion of vinyltrimethylsilane into cationic zirconium complexes [168–171]).

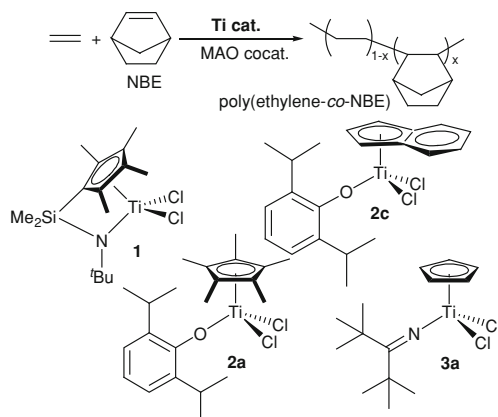
The Cp^* -aryloxo analogue (**2a**) incorporated vinyltrimethylsilane (VTMS) into polyethylene with moderate catalytic activities (Scheme 2.8, Table 2.7), and the resultant copolymers possessed high molecular weights with uniform molecular weight distributions. The Cp -ketimide analogue (**3a**) exhibited both higher catalytic activities and better VTMS incorporations than **2a** [163]. Efficient synthesis of high molecular weight copolymers with uniform compositions could be achieved by adopting **3a**, although both the activity and the M_n values seemed to decrease upon the increasing VTMS contents. The copolymerization by the constrained geometry catalyst (**1**) also proceeded efficiently (Copolymerization with α -olefin containing bulky substituents [79]).

More recently, the *tert*- BuC_5H_4 analogue (**2b**) exhibited rather efficient TBE incorporation in the copolymerization, whereas the Cp' -ketimide analogue (**3a**, **b**), constrained geometry catalyst (**1**), Cp_2ZrCl_2 did not incorporate TBE under the same conditions (Scheme 2.8, Table 2.7) [79]. Effect of both the cyclopentadienyl fragment (Cp') and the anionic donor ligands (Y) in $\text{Cp}'\text{TiX}_2(\text{Y})$ plays a crucial role for the successful copolymerization, as seen in the above copolymerization.

2.2.4 Copolymerization with Cyclic Olefins

Certain cyclic olefin copolymers (COCs) are amorphous materials with a promising combination of high transparency in the UV-Vis region along with humidity-, and heat-resistance (high glass transition temperature, T_g).^{2a–d} Three processes such as (1) ring-opening metathesis polymerization (ROMP) of multi-cyclic olefins and the subsequent hydrogenation, (2) coordination copolymerization of ethylene with cyclic olefins, (3) homopolymerization of cyclic olefins, are generally adopted for the practical production. In particular, the copolymerization route seems promising, because the desired properties can be tuned by their compositions (cyclic olefin contents etc.) as well as their microstructures (including tacticity).

Many examples were thus known for the copolymerization of ethylene with norbornene (NBE) using ordinary metallocenes [172–176], linked half-titanocenes (CGC) [56, 57, 120], half-titanocenes [84–87], and other so-called non-metallocenes [177–180]. However, successful examples for the efficient synthesis of random, high molecular weight copolymers with high NBE contents (>50 mol%), which possess high T_g (>150 °C), were limited. This is not only because both the activity and the molecular weights in the copolymer decrease upon increasing NBE contents, but also because the microstructure in the copolymer possessed few



Scheme 2.9 Copolymerization of ethylene with norbornene [84, 85]

NBE repeat units and contained alternating and/or isolated NBE inserted units due to the difficulty for repeated NBE insertion.

(Indenyl) $\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (**2c**) exhibited better NBE incorporation than the Cp^* -aryloxo analogue (**2a**), the 1,2,4- $\text{Me}_3\text{C}_5\text{H}_2$ -aryloxo analogue, and the constrained geometry catalyst (CGC, **1**), affording random copolymers with high NBE contents (Scheme 2.9) (Copolymerization with norbornene [84, 85]). The catalytic activity by the indenyl-aryloxo analogue initially increased upon increasing the NBE concentration charged, although the activity generally decreased upon increasing the NBE concentration [84].

The Cp-kemite analogue, $\text{CpTiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ (**3a**), exhibits both remarkable activity and efficient NBE incorporation for ethylene/NBE copolymerization [87]. As shown in Table 2.8, the activity increased upon increasing in initial NBE concentration, whereas the activities by other catalysts decreased upon increasing in NBE concentration. Note that the activity by **3a** increased at higher temperature (40, 60 °C) accompanied by increasing NBE content in the copolymer (due to a reduction in ethylene concentration in the mixture), and the activity did not decrease at least for 30 min. The resultant copolymers possessed high molecular weights with unimodal molecular weight distributions as well as with single compositions. The efficient synthesis of high molecular weight copolymers with high NBE contents (58.8–73.5 mol%) could be thus attained upon increasing the NBE concentration at low ethylene pressure (2 atm).

Both the activities and the NBE incorporations in the copolymerization by **3a** were not strongly affected by the Al cocatalyst employed (MAO, MMAOs), and the fact is a unique contrast to that reported in the copolymerization by $[\text{Me}_2\text{Si}(\text{fluorenyl})(\text{N}^t\text{Bu})]\text{TiMe}_2$ in which both the activity and the NBE incorporation are highly dependent upon the Al cocatalyst employed [181–184]. It is thus clear that these observed facts are significantly unique compared to those previously demonstrated in the copolymerization using ordinary metallocenes or linked half-titanocenes (Copolymerization with norbornene [86]).

Table 2.8 Copolymerization of ethylene with norbornene (NBE) by Cp*TiCl₂(O-2,6-*i*-Pr₂C₆H₃) [Cp* = Cp* (2a), indenyl (2c)], CpTiCl₂(N=C'Bu₂) (3a), [Me₂Si(C₃Me₄)(N'Bu)]TiCl₂ (1), [Me₂Si(indenyl)₂]ZrCl₂—MAO catalyst systems^a

Complex (μmol)	Temp/°C	Ethylene /atm	NBE ^b /mmol/mL	Activity ^c	M _n ^d × 10 ⁻⁴	M _w /M _n ^d	NBE ^e /mol%
Cp*TiCl ₂ (O-2,6- <i>i</i> -Pr ₂ C ₆ H ₃) 2a (0.2)	25	4	1.0	2640	29.6	1.46	21.7
(Ind)TiCl ₂ (O-2,6- <i>i</i> -Pr ₂ C ₆ H ₃) 2c (0.2)	25	4	1.0	2300	5.87	1.82	35.2
(Ind)TiCl ₂ (O-2,6- <i>i</i> -Pr ₂ C ₆ H ₃) 2c (0.2) ^f	25	2	2.5	678	3.91	1.58	58.8
CpTiCl ₂ (N=C'Bu ₂) 3a (0.02)	25	4	1.0	40200	71.9	2.92	40.7
CpTiCl ₂ (N=C'Bu ₂) 3a (0.02)	40	4	1.0	48900	62.0	2.37	45.9
CpTiCl ₂ (N=C'Bu ₂) 3a (0.02)	60	4	1.0	194000	47.5	2.20	51.2
CpTiCl ₂ (N=C'Bu ₂) 3a (0.02) ^f	25	2	10.0	31500	44.4	2.01	73.5
[Me ₂ Si(indenyl) ₂]ZrCl ₂ (0.10)	25	4	1.0	4860	22.9	2.37	29.5
[Me ₂ Si(C ₃ Me ₄)(N'Bu)]TiCl ₂ 1 (0.50)	25	4	1.0	2000	12.8	2.15	26.5

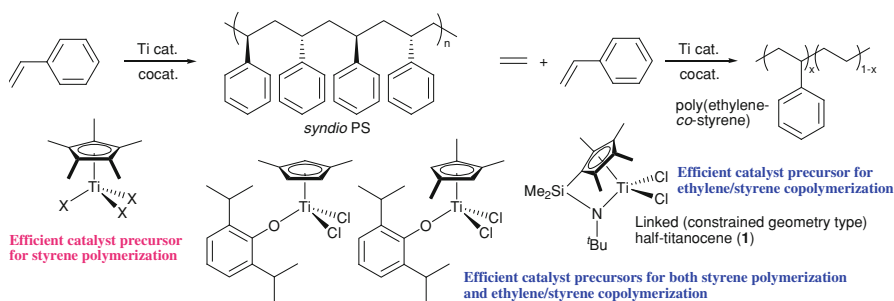
^a Cited from Ref. [86], Conditions toluene + NBE total 50 mL, MAO white solid (prepared by removing AlMe₃, toluene from PMAO) 3.0 mmol, 10 min
^b NBE concentration charged (mmol/mL)

^c Activity in kg-polymer/mol-M·h (M=Ti, Zr)

^d GPC data in *o*-dichlorobenzene versus polystyrene standards

^e NBE content (mol %) estimated by ¹³C NMR spectra

^f Conditions toluene + NBE total 10 mL



Scheme 2.10 Syndiospecific styrene polymerization and ethylene/styrene copolymerization by half-titanocenes [41, 42]

2.3 Syndiospecific Styrene Polymerization and Ethylene/Styrene Copolymerization Using Half-Titanocenes: Ligand Effects and Some New Mechanistic Aspects

Syndiotactic polystyrene (SPS) is a unique polymeric material due to its high melting point ($T_m=270\text{ }^{\circ}\text{C}$), high crystallinity, low density, low dielectric constant, and high chemical resistance toward organic solvents [10, 40, 109, 110, Example concerning syndiospecific styrene polymerization by half-titanocene complex—borate catalyst [185–187]]. This polymer cannot be prepared by free radical, anionic or ordinary Ziegler–Natta processes, but can be prepared by the syndio-specific polymerization using various half-titanocenes (Scheme 2.10), Cp^*TiX_3 or $\text{Cp}^*\text{TiX}_2(\text{Y})$ (Cp^* = cyclopentadienyl group; X = halogen, alkoxo, alkyl etc.; Y = anionic donor ligand) [10]. Ethylene/styrene co-polymers, which cannot be prepared by conventional (free radical, Ziegler–Natta) processes [10, See Reviews for linked half-titanocenes [16, 41, 42, 188–190]], also attract considerable attention [191–193], because styrene incorporation into the PE backbone results in drastic changes in the viscoelastic behavior as well as in the thermomechanical properties of the polymeric material [192].

Half-titanocenes such as Cp^*TiF_3 , $\text{Cp}^*\text{Ti}(\text{OMe})_3$ and $(\text{indenyl})\text{TiCl}_3$ are known to be efficient catalyst precursors for syndiospecific styrene polymerization ([10, 42, 111, 112, 188–194, Example concerning syndiospecific styrene polymerization by half-titanocene complex—borate catalyst 195–197]). However, these catalysts showed low activities in ethylene/styrene copolymerization and the resultant polymers afforded a mixture of polyethylene (PE), syndiotactic polystyrene (SPS) and the copolymer (E/S copolymer) (Examples in ethylene/styrene copolymerization [194–198]). In contrast, modified half-titanocenes of the type, $\text{Cp}^*\text{TiX}_2(\text{Y})$, are effective for both the styrene polymerization and ethylene/styrene copolymerization to afford the copolymers exclusively (Scheme 2.10) ([41, 42], Copolymerization with styrene with efficient styrene incorporation or in a living manner [90–95]). Linked half-titanocenes (so-called “constrained geometry type”) are

also effective for the copolymerization (See Reviews for linked half-titanocenes [15–17, 41, 42, 114, 115, 199–209], although these complexes generally exhibited extremely low catalytic activities for the styrene polymerization [199, 208]. Certain metallocenes and group 4 transition metal complexes, so-called post-metallocenes are also known to be effective for the copolymerization [210–216].

2.3.1 Syndiospecific Styrene Polymerization Using $Cp^*TiX_2(Y)$ –MAO Catalyst Systems

Modified half-titanocenes showed unique characteristics in ethylene copolymerizations (Reviews for nonbridged half-titanocenes [19, 20], Ethylene copolymerization with 2-methyl-1-pentene (disubstituted α -olefin [78–80, 82–95]), and it was demonstrated that an efficient catalyst for ethylene polymerization can be modified for efficient catalysts for syndiospecific styrene polymerization by the ligand modification (Cp^*) ([42], Copolymerization with styrene with efficient styrene incorporation or in a living manner [90]). Figure 2.2 summarizes the results for styrene polymerization using a series of $Cp^*TiCl_2(OAr)$ ($Ar = 2,6\text{-}^iPr_2C_6H_3$) and Cp^*TiCl_3 [$Cp^* = Cp$, 1,3- $Me_2C_5H_3$, C_5Me_5] complexes in the presence of MAO at various temperatures [217]. The activities by $Cp^*TiCl_2(OAr)$ increased at high temperature, and the activity with 16,000 kg-sPS/mol-Ti·h was attained with $Cp^*TiCl_2(OAr)$ at 85 °C. The activity at 70 °C increased in the order: $Cp > 1,3\text{-}Me_2C_5H_3 \gg 1,2,4\text{-}Me_3C_5H_2 > C_5Me_5$. The trend was the same as that by Cp^*TiCl_3 , suggesting that the activity was strongly affected by the nature of Cp^* : the observed trend was similar to that reported by Kaminsky [218]. The M_w values in the resultant SPS prepared by the aryloxo analogues increased in the order: $C_5Me_5 > 1,2,4\text{-}Me_3C_5H_2$, $1,3\text{-}Me_2C_5H_3 > Cp$. Although some M_w values were different from those by the trichloride systems, the order in the M_w values was similar to that by the trichloride systems [217]. It thus seems that the introduction of an electron-donating substituent on Cp^* was effective in obtaining of high molecular weight SPS [217]. The activity by $Cp^*TiCl_2(Y)$ was also affected by the anionic donor ligand (Y , Table 2.9) [42, 70, 217, 219, 220], and the activity at 70 °C increased in the order: $Y = O\text{-}2,6\text{-}Me_2C_6H_3 \gg OPh$, $O\text{-}4\text{-}MeC_6H_4$, $O\text{-}2,6\text{-}^iPr_2C_6H_3 > Cl$, $O\text{-}2,6\text{-}^iBu_2C_6H_3 > O\text{-}2\text{-}Me\text{-}6\text{-}\{(2,6\text{-}^iPr_2C_6H_3)N=CH\}C_6H_3 > O\text{-}2\text{-}^iBu\text{-}6\text{-}\{(2,6\text{-}^iPr_2C_6H_3)N=CH\}C_6H_3 > N=C^iBu_2$. The results clearly indicate that the substituent on the aryloxy (anionic donor) ligand *directly affects* the catalytic activity. Moreover, the M_w value for resultant SPS was also dependent upon the anionic ligand employed. These results suggest that aryloxo ligand play an important role toward both the activity and the M_w value.

Ordinary half-titanocenes such as Cp^*TiCl_3 , $Cp^*Ti(OMe)_3$, (indenyl) $TiCl_3$ are known to be efficient catalyst precursors for syndiospecific styrene polymerization in the presence of a co-catalyst [10, 40, 109, 110, 218, 221–226] (Fig. 2.2). Example concerning syndiospecific styrene polymerization by half-titanocene

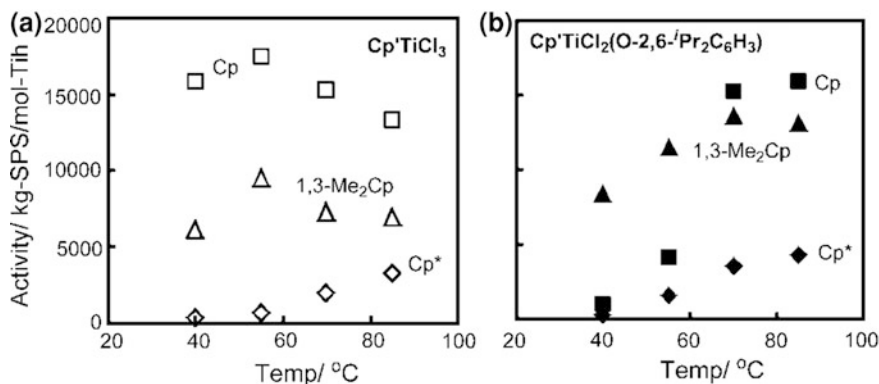


Fig. 2.2 Syndiospecific styrene polymerization by Cp^{*}TiCl₂(Y) [Y=Cl or OAr; Ar = 2,6-*i*Pr₂C₆H₃]—MAO catalyst systems. ^aCited from Ref. [217], *Conditions* complex 2.0 μmol, styrene/toluene = 10/20 mL, MAO white solid (Al/Ti = 1500, molar ratio), 10 min. **a** Cp^{*}TiCl₃—MAO catalyst systems; **b** Cp^{*}TiCl₂(2,6-*i*Pr₂C₆H₃)—MAO catalyst systems

Table 2.9 Effect of anionic donor ligand in styrene polymerization by Cp^{*}TiCl₂(Y)—MAO catalyst systems at 70 °C^a

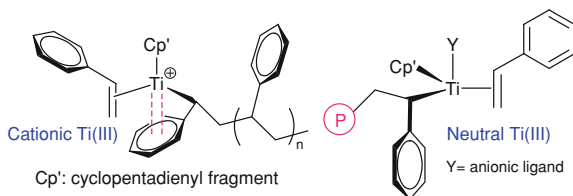
Y (anionic ligand)	Activity ^b	$M_w^c \times 10^{-4}$	M_w/M_n^c
Cl	1970	24.8	2.5
OC ₆ H ₅	4170	54.3	2.0
O-4-MeC ₆ H ₄	3750	26.7	2.4
O-2,6-Me ₂ C ₆ H ₃	9200	28.0	2.1
O-2,6- <i>i</i> Pr ₂ C ₆ H ₃	3600	49.0	2.2
O-2,6- <i>i</i> Bu ₂ C ₆ H ₃	1780	20.5	2.3
O-2-Me-6-[(2,6- <i>i</i> Pr ₂ C ₆ H ₃)N=CH]C ₆ H ₃	552	18.5	2.3
N=C ⁱ Bu ₂	222	19.1	2.1

^a Cited from Refs. [70, 217, 219, 220], *Conditions* complex 2.0 μmol, styrene/toluene = 10/20 mL, MAO white solid (Al/Ti = 1500, molar ratio), 10 min

^b Activity in kg-sPS/mol-Ti-h

^c GPC data in *o*-dichlorobenzene versus polystyrene standards

Scheme 2.11 Proposed catalytically-active species for syndiospecific styrene polymerization [38]



complex—borate catalyst [185–187], Examples of a mechanistic studies for styrene polymerization [227–229]). The oxidation state of the active species has been invoked as cationic Ti(III) (Scheme 2.11, left) ([218, 221–226], Example

concerning syndiospecific styrene polymerization by half-titanocene complex—borate catalyst [185–187, 191–193], whereas the cationic Ti(IV) species would play a role for the ethylene/styrene copolymerization ([41], Related publications for synthesis and reactivity of cationic half-titanocene alkyl complexes containing aryloxo ligand [97, 98], [220]). In contrast, Tomotsu (Idemitsu) insisted a possibility that neutral Ti(III) species [226], $[\text{Cp}^*\text{Ti}(\text{R})(\text{Y})(\text{styrene})]$ (Y = anionic ligand), should play a role as the active species (Scheme 2.11, right) [10, 40–42]. On the basis of the above results, it is clear that both Cp^* and Y play an essential role for exhibiting high activity and for affording high molecular weight polymer with unimodal molecular weight distribution. Since the role of anionic donor ligand toward both the activity and the molecular weight is present, if the possibility that neutral Ti(III) or cationic Ti(IV) species plays a role for this polymerization.

2.3.2 Ethylene/Styrene Copolymerization Using Half-Titanocenes

Half-titanocenes, Cp^*TiX_3 ($\text{X}=\text{F}$, OMe etc.), which are efficient catalyst precursors for syndiospecific styrene polymerization ([10, 40, 109, 110, 218, 221–226], Example concerning syndiospecific styrene polymerization by half-titanocene complex—borate catalyst [185–187]), afforded a mixture of polyethylene (PE), syndiotactic polystyrene (SPS) and the copolymer (E/S copolymer) in the ethylene/styrene (co)polymerization (Copolymerization with styrene with efficient styrene incorporation or in a living manner [93], The product distribution and the [194–198]). The product distribution and the activity in (co)polymerization using a Cp^*TiX_3 –MAO catalyst system is thus highly sensitive to the anionic donor ligand ($\text{X}=\text{Cl}$, CH_2Ph , OCH_3 , OCH_2Ph etc.), the reaction conditions, the nature of MAO (Examples in ethylene/styrene copolymerization [196, 197]), and the exact mixing sequence and pre-contact time. These factors usually lead to poor reproducibility. $\text{Cp}^*\text{Ti}(\text{CH}_2\text{Ph})_3$ – $\text{B}(\text{C}_6\text{F}_5)_3$ afforded E/S copolymer including PE and SPS, and the distributions were dependent upon the polymerization temperature, the pretreatment procedure (Table 2.10) (Examples in ethylene/styrene copolymerization [195]). The resultant copolymer possessed an alternating sequence, and no resonances ascribed to styrene repeating units were seen. However, it seems very difficult to find suitable conditions for the exclusive preparation of E/S copolymer (Table 2.10), and selective co-oligomerization proceeded in the presence of Cp^*TiCl_3 ($\text{Cp}^*=\text{Cp}$, Cp^* , indenyl)– $\text{B}(\text{C}_6\text{F}_5)_3$ (MAO) catalyst systems under certain conditions [230, 231].

Table 2.10 Ethylene/styrene copolymerization using $\text{Cp}^*\text{Ti}(\text{CH}_2\text{Ph})_3\text{-B}(\text{C}_6\text{F}_5)_3\text{-Al}^i\text{Bu}_3$ catalyst^a

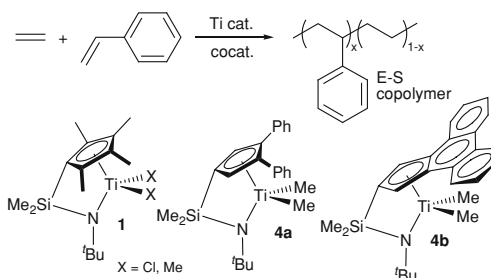
Temp. /°C	Styrene /mol/L	Yield /g ^b	Activity ^c	Composition (wt%) ^d		
				PE	E/S	SPS
0	1.1	0.30	48	>90		
25	0.8	0.45	72	63	22	15
50	0.4	0.35	56	33	58	9
50	1.2	0.49	78	6	72	22
50	2.0	1.00	160	8	20	72
75	0.5	0.35	56	29	41	30

^a Cited from Ref. [195], Conditions $\text{Cp}^*\text{Ti}(\text{CH}_2\text{Ph})_3/\text{B}(\text{C}_6\text{F}_5)_3/\text{Al}^i\text{Bu}_3 = 25/25/25 \mu\text{mol}$, ethylene 1 atm, toluene + styrene total 26 mL

^b After removal of atactic polystyrene

^c Activity in kg-polymer/mol-Ti·h

^d Estimated from ^{13}C NMR spectra

Scheme 2.12 Selective linked half-titanocenes for ethylene/styrene copolymerization [129]**Table 2.11** Copolymerization of ethylene with styrene using different linked half-titanocenes—MAO catalyst systems^a

Complex	Activity ^b	$M_w^c \times 10^{-4}$	M_w/M_n^c	Styrene ^d /mol%
1 (X=Me)	23700	1.13	2.36	11.0
4a	61000	7.28	4.76	21.5
4b	99400	13.4	5.26	30.6

^a Cited from Ref. [201], Conditions complex 3.0 μmol , styrene 455 g, toluene 433 g, ethylene 200 psi (13.6 atm), H_2 50 psi, $\text{B}(\text{C}_6\text{F}_5)_3$ 3.0 μmol , 90 °C, 30 min

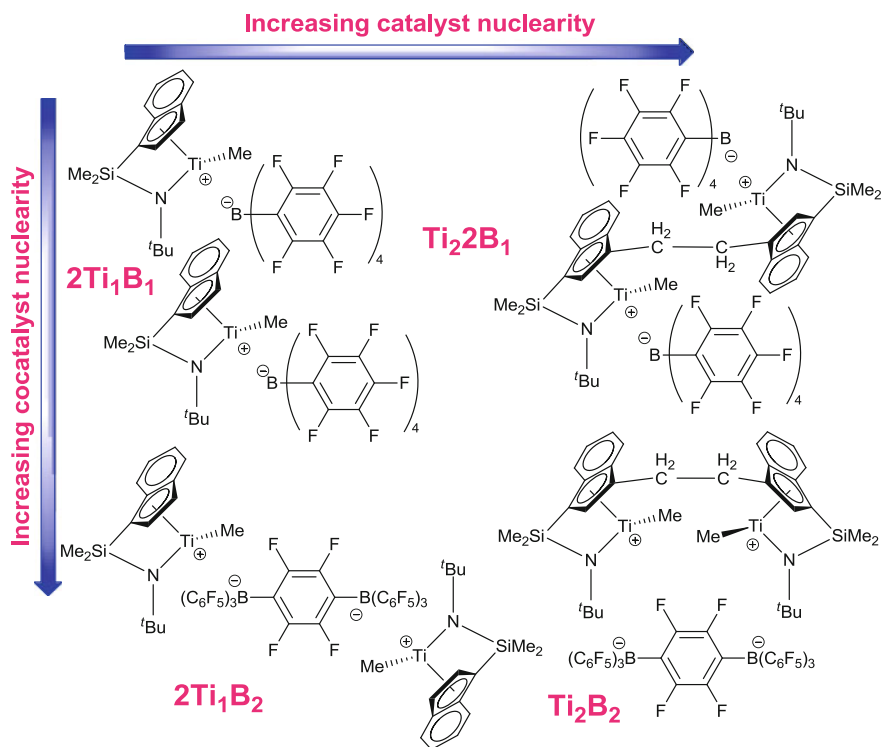
^b Activity in kg-polymer/mol-Ti·h

^c GPC data in *o*-dichlorobenzene versus polyethylene standards

^d Styrene content in E/S copolymer estimated by ^1H NMR spectra

2.3.2.1 Recent Results in Ethylene/Styrene Copolymerization by Linked (Constrained Geometry Type) Half-Titanocenes

Linked half-titanocenes like $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ (**1**, constrained geometry catalyst, CGC) are known to be efficient catalyst precursors for the copolymerization (Reviews for linked half-titanocenes, see [15–17, 199–207]), although



Scheme 2.13 Catalyst/cocatalyst nuclearity matrix for constrained geometry catalysts [124]

they exhibited extremely low activity for the styrene polymerization [199, 208]. The styrene incorporation is generally invariably <50 mol%, regardless of the styrene/ethylene feed ratio (Reviews for linked half-titanocenes, see [15–17, 199–207]). It has been known that the cyclopentadienyl fragment affected both the activity and the styrene incorporation [202–204]. The amide substituent was also effective for the styrene incorporation [206, 207], and notable styrene incorporation was attained with $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{NCy})]\text{TiCl}_2$ [207]. Complexes **4a,b** shown in Scheme 2.12 showed a significantly better efficiency than catalyst **1** ($\text{X}=\text{Me}$) (Table 2.11) [201]: **4b** showed better both activity and efficient styrene incorporation than **4a** under the same conditions.

As described above, mononuclear linked half-titanocenes (CGCs) showed extremely low activity for styrene polymerization, and the styrene content in the resultant copolymer did not exceed 50 mol%. In contrast, the bimetallic system (**Ti₂2B₁** or **Ti₂2B₂** in Scheme 2.13) exhibited significantly higher catalytic activities for styrene polymerization than the mononuclear system (**2Ti₁B₁** or **2Ti₁B₂**), although the resultant polymer possessed *atactic* stereoregularity (Table 2.12) (Reviewing article for nuclearity and cooperativity effects in binuclear catalysts and cocatalysts for olefin polymerization [124, 208, 209].

Table 2.12 Styrene polymerization and ethylene/styrene copolymerization catalyzed by mono-nuclear or dinuclear linked half-titanocenes—cocatalyst systems^a

Cat.	Styrene/toluene (mL/mL)	Ethylene / atm	Time /h	Activity ^b	$M_w^c \times 10^{-4}$	M_w/M_n^c	Styrene / mol% ^d
Ti₁ + B₁	5/25	—	3	2.7	11.96	1.84	100
Ti₂ + B₂	5/25	—	3	104	1.04	1.44	100
Ti₂ + B₁	5/25	—	3	112	0.80	1.47	100
Ti₂ + B₁	10/50	1.0	1	259	35.8	1.82	39
Ti₂ + B₁	20/40	1.0	1.5	194	47.1	1.33	50
Ti₂ + B₁	30/30	1.0	0.5	384	43.8	2.40	66
Ti₂ + B₁	60/0	1.0	0.5	312	47.9	1.72	76

^a Cited from Refs. (Reviewing article for nuclearity and cooperativity effects in binuclear catalysts and cocatalysts for olefin polymerization [124, 208, 209]), *Conditions* **Ti₁** (10 μ mol) or **Ti₂** (5 μ mol) + **B₁** (10 μ mol) or **B₂** (5 μ mol), 20 °C, ethylene 1.0 atm

^b Activity in kg-polymer/mol-Ti·h

^c By DSC thermograms

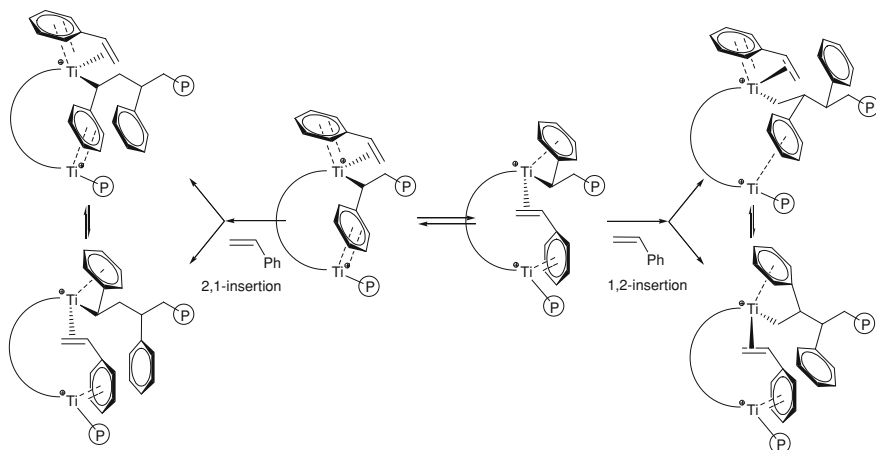
^d GPC data in *o*-dichlorobenzene versus polystyrene standards

^e Estimated by ¹³C NMR spectra

A drastic improvement in the styrene incorporation in the copolymerization could be achieved by using a dinuclear catalyst system (**Ti₂2B₁**), synthesis of a copolymer with a high styrene content (76 mol%) has thus been achieved in this catalysis (Table 2.12). Although the observed activities should be further improved, this catalyst system afforded broad range controllable styrene incorporation (styrene contents 39–76 mol%) (Reviewing article for nuclearity and cooperativity effects in binuclear catalysts and cocatalysts for olefin polymerization [124]). Resonances ascribed to the three head-to-tail coupled styrene units in addition to tail-to-tail coupled dyads were observed in the ¹³C NMR spectra of the copolymers (styrene > 50 mol%) [208]. It was assumed that the arene ring of the last-inserted styrene may preferentially coordinate to the adjacent Ti center in the bimetallic **Ti₂** (Scheme 2.14), thus reducing coordinative saturation at the polymerization site and accelerating homopolymerization (Reviewing article for nuclearity and cooperativity effects in binuclear catalysts and cocatalysts for olefin polymerization [124], 218]. The coordinated arene rings can, in principle, participate in several types of multimetallic/enchainment-altering interaction.

2.3.2.2 Ethylene/Styrene Copolymerization by Modified Half-Titanocenes, Cp'TiX₂(Y)

The aryloxo modified half-titanocenes, Cp'TiX₂(O-2,6-*i*-Pr₂C₆H₃) (X=Cl, Me) exhibited high catalytic activities for ethylene/styrene copolymerization in the presence of MAO, affording poly(ethylene-*co*-styrene)s exclusively without PE and/or SPS as by-products (Table 2.13) (Copolymerization with styrene with



Scheme 2.14 Proposed pathways in the ethylene/styrene copolymerization [124]

Table 2.13 Ethylene/styrene copolymerization by $\text{Cp}^*\text{TiCl}_2(\text{OAr})$ [$\text{Cp}^* = 1,2,3\text{-Me}_3\text{C}_5\text{H}_2$, $1,3\text{-Me}_2\text{C}_5\text{H}_3$, $\text{tert-BuC}_5\text{H}_4$; $\text{OAr} = \text{O-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3$] or $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^i\text{Bu})]\text{TiCl}_2\text{-MAO}$ catalyst systems^a

Complexes	Styrene / mL	Activity ^b	E/S copolymer (THF soluble)			
			content ^c / wt%	$M_w^d \times 10^{-4}$	M_w/M_n^d	Styrene / mol% ^e
$(1,2,3\text{-Me}_3\text{C}_5\text{H}_2)\text{TiCl}_2(\text{OAr})$	3	4100	99.1	17.0	1.6	26.0
$(1,2,3\text{-Me}_3\text{C}_5\text{H}_2)\text{TiCl}_2(\text{OAr})$	5	3070	98.3	11.0	1.7	38.8
$(1,2,3\text{-Me}_3\text{C}_5\text{H}_2)\text{TiCl}_2(\text{OAr})$	10	2720	97.8	6.6	1.6	51.2
$(1,2,3\text{-Me}_3\text{C}_5\text{H}_2)\text{TiCl}_2(\text{OAr})^f$	15	1850	90.4	3.6	2.1	73.6
$(1,3\text{-Me}_2\text{C}_5\text{H}_3)\text{TiCl}_2(\text{OAr})$	10	4140	98.2	3.7	1.6	49.0
$(^t\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{OAr})$	10	1840	98.7	3.5	2.2	51.2
$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^i\text{Bu})]\text{TiCl}_2$	10	5630	99.6	18.0	1.8	32.7

^a Cited from Ref. [91], Conditions complex 1.0 μmol (2.0 $\mu\text{mol/mL}$ -toluene), ethylene 4 atm, total volume of toluene and styrene = 30 mL, MAO white solid (Al/Ti = 2000, molar ratio), 25 °C, 10 min

^b Activity in kg-polymer/mol-Ti·h, polymer yield in acetone insoluble fraction

^c Percentage of content in copolymer based on polymer obtained (acetone insoluble, THF soluble fraction)

^d GPC data in *o*-dichlorobenzene versus polystyrene standards

^e Styrene content (mol%) in copolymer by ^1H NMR (1,1,2,2- $\text{C}_2\text{D}_2\text{Cl}_4$)

^f Conducted under ethylene 2 atm

efficient styrene incorporation or in a living manner [90, 91]). The resultant copolymers possessed not only relatively high molecular weights with unimodal molecular weight distributions, but also single composition as confirmed by DSC

thermograms, CFC and GPC/FT-IR (Copolymerization with styrene with efficient styrene incorporation or in a living manner [91]). The activities decreased slightly with an increase in the styrene concentration, whereas the styrene contents in the copolymers increased upon increasing the [S]/[E] initial feed molar ratios. Styrene incorporations with aryloxo analogues is more efficient than that with $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ (**1**, $\text{X}=\text{Cl}$). Thus, the present catalysis provides an efficient synthesis of copolymer with high styrene content, especially higher than 50 mol%, in a random manner. The microstructure analysis in the resultant E/S copolymers by ^{13}C NMR spectra indicated that the copolymer prepared by $(1,2,3\text{-Me}_3\text{C}_5\text{H}_2)\text{TiCl}_2(\text{O-}2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ possesses resonances ascribed to two or three styrene repeat units connected via head-to-tail coupling, in addition to the resonances ascribed to tail-to-tail coupling of a styrene unit or head-to-head bridged by an intervening ethylene unit. This is especially interesting in contrast to the results with the linked half-titanocene (**1**) ([40], Copolymerization with styrene with efficient styrene incorporation or in a living manner [90, 91]).

The copolymerization by $\text{Cp}^*\text{TiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ (**3b**) took place in a living manner in the presence of MAO co-catalyst, although the homopolymerization of ethylene and styrene did not proceed in a living manner [92]. No styrene repeating units were observed in the resultant copolymers, suggesting that a certain degree of styrene insertion inhibits chain transfer in this catalysis. The living nature was maintained under various conditions (Al/Ti molar ratios, ethylene pressure, styrene concentrations, temperature) (Copolymerization with styrene with efficient styrene incorporation or in a living manner [93]). Copolymerization with $\text{CpTiX}_2(\text{N}=\text{PCy}_3)$ (**5**, $\text{X}=\text{Cl}$, Me)-cocatalyst (MAO, borates) systems proceeded with notable catalytic activities [at 60–90 °C, ethylene 70 psi (4.76 atm), [S]/[E] = 12] [76], however, the styrene incorporation seemed less efficient than with either aryloxo analogues or linked half-titanocene [styrene content: 33.4–61.4 wt% (<27.6 mol%)] [76, 232].

Taking into account the above results, it is clear that modified half-titanocenes, $\text{Cp}^*\text{TiX}_2(\text{Y})$, are better catalyst precursors for synthesis of ethylene/styrene copolymers in high yields. It was also clear that both the activity and the styrene incorporation are dependent upon the type of ligands employed (Cp^* and Y). These complexes are also effective for not only ethylene polymerization, but also syndiospecific styrene polymerization: the results are in unique contrast to those with ordinary half-titanocenes, Cp^*TiX_3 . Therefore, these catalysts may be suitable for mechanistic study on syndiospecific styrene polymerization as well as copolymerization, as described below ([41], Copolymerization with styrene with efficient styrene incorporation or in a living manner [93, 94]).

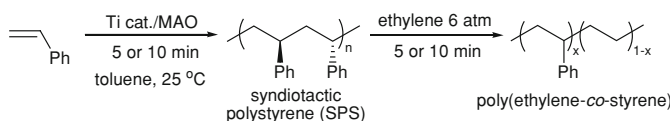
2.3.3 Role of Anionic Donor Ligand in Ethylene/Styrene Copolymerization and Syndiospecific Styrene Polymerization: Mechanistic Considerations

Ethylene/styrene copolymerizations using three half-titanocenes containing Cp* ligand of type, Cp*TiX₂(Y) [X=Cl, Y=O-2,6-*i*Pr₂C₆H₃, Cl; X=Me, Y=O-2,6-*i*Pr₂C₆H₃, Me]—cocatalyst systems were used under the same conditions [93]. The copolymerizations with Cp*TiCl₂(OAr) (**2a**) gave copolymers with high styrene contents (31.9–34.3 mol%), and significant increase in the activity was not observed at high temperature. The resultant copolymers prepared by **2a** possessed lower M_n values with unimodal distributions ($M_w/M_n = 1.50$ – 1.62). In contrast, the polymers prepared with the trichloride analogue, Cp*TiCl₃, showed bimodal molecular weight distributions consisting of a mixture of PE and SPS, and the proportion of SPS increased at high temperature due to an increase in the activity for syndiospecific styrene polymerization (for syndiospecific styrene polymerization [91, 217]). Copolymerization using the aryloxy-dimethyl analogue, Cp*TiMe₂(OAr)–MAO or [PhN(H)Me₂][B(C₆F₅)₄] (AFPB) catalyst system afforded the copolymer exclusively [93]. In contrast, the polymer prepared with the Cp*TiMe₃–AFPB catalyst was PE (containing a trace amount of the copolymer with low styrene content) or the copolymer with an extremely low styrene content, whereas the copolymerization in the presence of MAO afforded a mixture of PE and SPS, as observed in the (co)polymerization using Cp*TiCl₃. The fact that no SPS was formed in polymerization with Cp*TiMe₃–AFPB catalyst was analogous to the fact that Cp*Ti(CH₂Ph)₃–AFPB catalyst did not afford SPS in an attempted styrene polymerization (under dark conditions), and only poly(propylene-*co*-styrene) oligomer was formed in the propylene/styrene copolymerization [227–229].

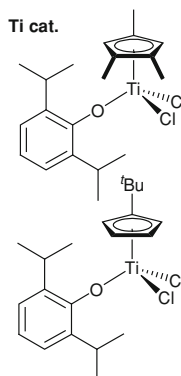
These results strongly suggest that cationic Ti(IV) species play an important key role in the ethylene polymerization as well as the ethylene/styrene copolymerization. These results also suggest that another catalytically-active species [likely Ti(III)] for syndiospecific styrene polymerization is formed in the presence of MAO (Copolymerization with styrene with efficient styrene incorporation or in a living manner [93]).

Exclusive formation of copolymers without formation of SPS as a by-product was observed with the introduction of ethylene into a solution of syndiospecific styrene polymerization using Cp'TiCl₂(O-2,6-*i*Pr₂C₆H₃) (Cp'=*i*BuC₅H₄, 1,2,4-Me₃C₅H₂)—MAO catalysts (Scheme 2.15). Note that the activities and the M_w values as well as the styrene contents in the latter copolymerizations were identical to those in their independent runs. These results clearly indicate that the active species for the syndiospecific styrene polymerization can be tuned to the active species for copolymerization [94, 233]. In contrast, styrene polymerization did not proceed when ethylene was removed from the reaction mixture of ethylene/styrene copolymerization (likely due to oxidation upon exposure to ethylene) (Copolymerization with styrene with efficient styrene incorporation or in a living manner [94]) (Table 2.14).

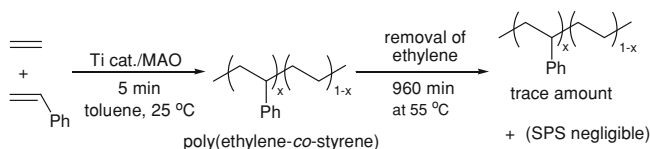
Introduction of ethylene after syndiospecific styrene polymerization



Ti cat.



Removal of ethylene after ethylene/styrene copolymerisation

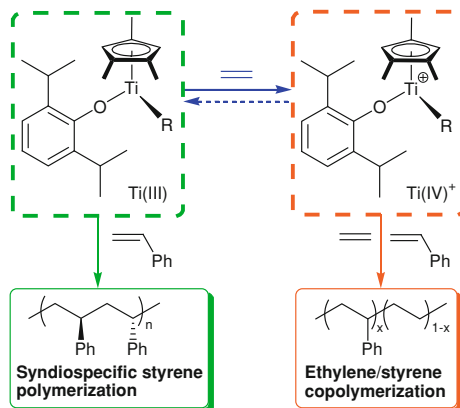
**Scheme 2.15** Step (co)polymerization of ethylene with styrene [94]**Table 2.14** Copolymerization of ethylene with styrene by $\text{Cp}^*\text{TiCl}_2(\text{Y})$ [$\text{Y}=\text{O}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3(\text{OAr}), \text{Cl}$ —MAO catalyst systems]^a

Complex Y	Temp. /°C	Composition ^b (%)			Activity ^c (%)	Styrene Cont. ^d /Mol%	$M_n^e \times 10^{-4}$	M_w^e/M_n^e
		E-S	PE	SPS				
OAr	25	>99	tr.	tr.	504	31.9	9.28	1.62
OAr	40	>98	tr.	tr.	660	34.3	9.79	1.50
Cl ^f	25	tr.	86.8	13.2	250	>99 ^g	5.85	1.26
						—	0.29	2.69
Cl ^f	40	tr.	81.6	18.4	280	>99 ^g	5.07	1.31
						—	0.31	1.75
Cl ^f	55	tr.	69.8	30.2	260	>99 ^g	3.56	1.48
						—	0.21	1.77

^a Cited from Ref. [93], Conditions catalyst 2.0 μmol , MAO white solid 3.0 mmol, ethylene 6 atm, styrene 10 mL, styrene + toluene total 30 mL, 10 min^b Based on a mixture of PE, SPS and copolymer. (acetone insoluble fraction)^c Activity in kg-polymer/mol-Ti-h^d Styrene content (mol%) estimated by ¹H NMR spectra^e GPC data in *o*-dichlorobenzene versus polystyrene standards.^f Resultant polymers were a mixture of PE and SPS^g Confirmed by GPC/FT-IR, ¹³C NMR spectra, DSC thermograms

Taking the results into account [93], it seems likely that the cationic Ti(IV) species, $[\text{Cp}^*\text{Ti(L)R}]^+$, play a role in the copolymerization and the active species containing an anionic ancillary donor ligand [assumed to be neutral Ti(III) , $\text{Cp}^*\text{Ti(L)R}$] proposed by Tomotsu et al. [226] plays a role in the syndiospecific styrene polymerization (Scheme 2.16) (Copolymerization with styrene with efficient styrene incorporation or in a living manner [94]). These results should also explain the reported findings that the activities and molecular weight of the resultant syndiotactic polystyrene in styrene polymerization using

Scheme 2.16 Proposed catalytically-active species for syndiospecific styrene polymerization and ethylene/styrene copolymerization [41, 93]



$\text{Cp}'\text{TiX}_2(\text{Y})$ —cocatalyst systems were highly dependent upon the anionic donor ligand (Y) [93, 94, 233]. These proposals are in contrast to the hypothesis that cationic Ti(III) species, $[\text{Cp}'\text{Ti}(\text{R})(\text{styrene})]^+$, play a role as the catalytically-active species for the styrene polymerization using $\text{Cp}'\text{TiX}_3$. This hypothesis should help to explain why polystyrene structures in the resultant copolymers prepared with $\text{Cp}'\text{TiCl}_2(\text{Y})$ —MAO catalysts are atactic.

2.4 Summary and Outlook

As described above, it is now clear that *nonbridged* modified half-titanocenes containing anionic ancillary donor ligand of the type, $\text{Cp}'\text{TiX}_2(\text{Y})$, displayed unique characteristics that are different from those especially by ordinary catalysts (Ziegler-Natta, metallocenes, linked half-titanocenes). Ligand modifications (Cp' , Y) are very important especially for the successful copolymerizations (with both remarkable activities and efficient comonomer incorporation) [19, 20]. As demonstrated above (Copolymerization with styrene with efficient styrene incorporation or in a living manner, [90]). Equilibrium constants for alkene coordination to $(\text{MeC}_5\text{H}_4)_2\text{Zr}^+(\text{O}^t\text{Bu})(\text{ClCD}_2\text{Cl})$ [167]. See For reported examples of insertion of vinyltrimethylsilane into cationic zirconium complexes [168–171], the efficient catalyst precursors for ethylene polymerization can be tune to the efficient catalyst precursors for syndiospecific styrene polymerization by simple modification of cyclopentadienyl fragment: this is one of the unique characteristics for using this catalysis. Fine tuning of anionic donor ligand is also important for exhibiting high (with better stability in the catalytic reaction) as well as with better comonomer incorporation. Several promising findings that should be very important from both academic and industrial viewpoints have been demonstrated, and these efforts will pave new promising possibilities for evolution of new *fine* polyolefins with unique properties by incorporation of new comonomers and/or by adopting new synthetic strategies.

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